## The Cohesive Energy Density of Polymer Melts: Calculation and Use

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The Cohesive Energy Density (CED) of polymer melts is of great importance in the description of the thermodynamic properties of polymer systems. For low molecular weight liquids, the CED can be computed using the energy of vaporization and the density. The solubility parameter,  $\delta$ , is the square root of the CED. Differences in solubility parameters are key measures of the miscibility of polymer-polymer and polymer-solvent mixtures. Since polymer molecules have vanishingly small vapor pressures, one cannot directly measure the energy of vaporization. This has led to the use of many approximation techniques for the estimation of the CED for use in calculations ranging from phase diagrams to bulk properties such as surface tension. The internal pressure,  $(\partial U/\partial V)_T$ , is commonly used as a measure of the CED for many equation of state applications. The ratio of the internal pressure to the CED is a molecular weight and temperature dependent quantity which can be in the range 1.1 to 1.5 for low molecular weight liquids. These 10 to 50% errors involved with using the internal pressure as a measure of the CED are rarely discussed by those who use equation of state to model the phase behavior of polymer systems.

We describe two methods that can be used to calculate the CED for polymer molecules. The first requires the CED for low molecular weight oligomers of the polymer and makes use of the linearity of the CED as a function of inverse molecular weight. Oligomers of polyethylene are used to illustrate the calculation. A second more widely applicable method uses surface tension measurements and bulk thermodynamic properties to predict the CED. These calculated CED's can then be used to predict phase properties and other thermodynamic properties that depend on the CED of the liquid. Using the CED and the ideal specific heat,  $C_p^o$ , of the polymer, we can completely specify the thermodynamic properties of the polymer melt. The ideal specific heat of the polymer can be calculated from either the ideal specific heat data for oligomers of the polymer or measured specific heat data in conjunction with the CED data for the polymer. Using pressure, volume, and temperature data for the polymer melt, the ideal specific heat, and the CED, we perform calculations of enthalpy and entropy differences for polymer melts.